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NMR study of intermolecular reorientation in p-dimethyl amino benzaldehyde

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NMR study of *p*-dimethyl amino benzaldehyde $(CH_3)_2N\,C_6H_4CHO$ has been made in order to gain information concerning the rotational motion of methyl groups together with the possible internal rotation of aldehyde group. NMR measurements were performed over the temperature range from 77°K to 313°K. The analysis of the experimental data shows the reorientation of the methyl group at room temperature. The reorientation of aldehyde group was observed at 310°K.

1. INTRODUCTION

In the present investigation authors have observed that *p*-dimethyl amino benzaldehyde containing substituent groups shows a remarkable effect on the value of second moment with the rise in temperature. In the absence of any precise data regarding the molecular structure of *p*-dimethyl amino benzaldehyde a model of compound assuming the standard values of the bond distances and angles was constructed. Structural parameters from other molecules such as benzene derivative and aldehyde have also been a basis for the choice.

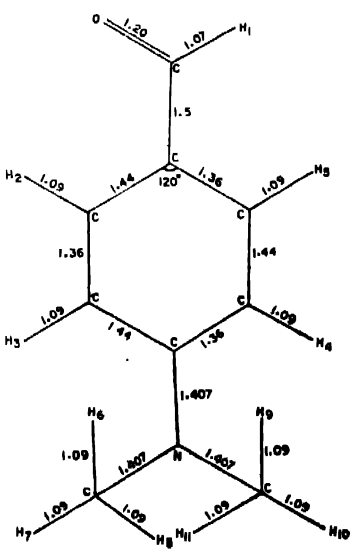

Fig. 1. Molecular structure of *p*-dimethyl amino benzladehyde.

The ring group was assumed unsymmetrical with the bond distances C–C = 1.36 Å and 1.44 Å alternately, and C–H = 1.09 Å. The C–C bond connecting the aldehyde group was assumed to be 1.50 Å with C–O = 1.201 Å, C–H = 1.7 Å, ∠ CCH = 124°6′ and ∠ CCO = 123°2′. The C–N bond distance = 1.407. The molecular structure is shown in figure 1.

2. Experimental Details

The NMR experiment was performed using a Varian Associates variable frequency spectrometer and an associated nuclear induction probe with a 12″ magnet system. The assumed frequency was 7.5 Mc/s. The derivative of the dispersion signals was observed by means of a Varian model V-4340 output control unit amplifier and a phase sensitive detector. The experiment was performed over temperature range from 77°K to 313°K, since *p*-dimethyl amino benzaldehyde sublimes rapidly investigation at very high temperature could not be carried out.

3. Calculations

The intramolecular second moment S_1 of *p*-dimethyl benzaldehyde was calculated with the help of Van Vleck's (1948) equation

$$S_1 = \frac{715.9}{N} \sum_{j>k} r_{jk}^{-6},$$

where N is the number of the magnetic nuclei over which the sum is taken and r_{jk} is the internuclear vector between nuclei j and k. S_1 for the sample was found to be 10.58 gauss^2.

The intermolecular contribution to the second moment for *p*-dimethyl benzaldehyde was calculated following the method adopted by Andrew & Eades (1953), and was found to be 9.5 gauss^2. The value seems to be reasonable as the intermolecular contribution to the second moment for 2-4 dimethoxy benzaldehyde calculated by Mirza *et al* (1972), which has almost the same number of magnetic nuclei distributed in almost similar manner is 8.5 gauss^2. The small difference between these two values of the intermolecular second moment may be accounted for by the difference in the positions of groups present in the compound. Hence theoretical rigid lattice second moment is found to be 10.58+9.2 = 20.78 gauss^2.

4. Discussion

At 77°K the mean value of experimental second moment is 19.98 gauss^2 which is in good agreement with the theoretically calculated value. This implies that the lattice is effectively rigid at lower temperature.

The variation of second moment against temperature is shown in figure 2. The value of second moment at room temperature 295°K was reduced to 10.98 gauss^2. Alpert (1949) and Gutowsky & Pake (1950) studied in detail the effect of motion in the lattice following the theory given by Bloembergen *et al* (1948).

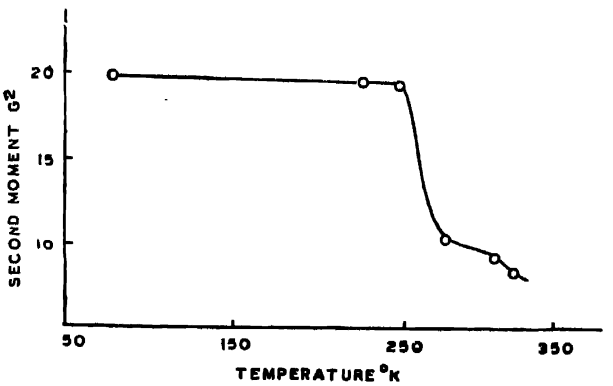

Fig. 2. Variation of second moment with temperature.

According to Pake the value of second moment falls by a factor four of its rigid lattice value due to the reorientation of triangular group about the symmetry axis for *p*-dimethyl amino benzaldehyde. Applying the theory of Pake reduction was 10.39 which is in good agreement with the experimentally calculated value 10.98 gauss^2. The reduction in the value of second moment at room temperature may be accounted for by the reorientation of the methyl group about the axis of symmetry. When the temperature is raised above the room temperature the value of second moment falls slightly and reaches 8.5 G^2. There are two possibilities to account for this reduction.

(1) The rotation of the aldehyde group. (2) The molecular reorientation about the axis of symmetry. The possibility of molecular reorientation is completely ruled out due to failry large size of molecule and also disagreement with the theory given by Gutowsky & Pake (1950).

The torsional frequency for benzaldehyde was found to be 113.8 cm^{-1} by Kakkar & Rinehart (1970). The barriers to the internal rotation of the aldehyde group as calculated from this frequency is 4.9 Kcal/mol. A rough estimate of activation energy can be made with the help of approximate formula $E = 37$ Tc (Waugh *et al* 1963) where T_c is the transition temperature. Taking T_c as 310°K (approx.) the value of E comes out to be 11.4 Kcal/mol. This much of energy acquired by the aldehyde group is sufficient to overcome the height of the potential barrier and consequently the aldehyde group is most likely to rotate about C–C axis.

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REFERENCES

Alpert N. L. 1949 *Phys. Rev.* **75**, 398.
Andrew E. R. & Eades R. G. 1953 *Proc. Roy. Soc.* (London), **A216**, 398.
Bloembergen N., Pound R. V. & Purcell E. C. 1948 *Phys. Rev.* **73**, 679.
Gutowsky H. S. & Pake G. E. 1950 *J.C.P.* **18**, 162.
Kakkar P. K. & Rinehart E. A. 1970 *J. Chem. Phys.* **52**, 407, 3803.
Mirza P. 1972 *Ind. J. Phys.* **46**, 508, 512.
Van Vleck J. H. 1948 *Phys. Rev.* **74**, 1168.
Waugh J. S. & Tsang T. 1962 *Phys. Rev.* **128**, 2639.